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Purification of medical ^{153}Sm using radiation-resistant ionic liquids

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Several radioisotopes of elements of the lanthanide series, like ^{153}Sm, are being applied in the field of therapeutic radiopharmaceuticals. These radiolanthanides are mainly being used for treatment of different types of bone cancer because of their favorable physical decay properties since they consist of β^- emitting radioisotopes. Moreover, they can also be used for bone imaging with the use of γ-ray detectors because of the emission of γ-photons during decay. The ^{153}Sm radionuclide is produced via neutron irradiation of a target of enriched ^{152}Sm, i.e. ^{152}Sm(n,γ)^{153}Sm ($t_{1/2}$ = 46.284 h). The stable ^{153}Eu isotope is formed via subsequent β^- decay of ^{153}Sm, which can be excreted by the human body without causing additional problems. The ^{153}Sm radioisotope can be produced in the BR2 reactor, considered as a major facility for routine supply of radioisotopes, available at the Belgian Nuclear Research Institute (SCK•CEN). This production is characterized by high specific activities, i.e. 4500 Ci ^{153}Sm per gram of ^{152}Sm. Enriched samarium targets are irradiated during 4 days in a thermal neutron flux of 3.5 x 10^{14} n/cm²s, being carried out in dedicated in-core devices within standard irradiation cycles of 3-4 weeks. BR2's current annual operating regime is based on five irradiation cycles.[1] This high neutron flux is needed to ascertain the specific activity of the ^{153}Sm radioisotope. ^{154}Eu ($t_{1/2}$ = 8.593 y) is also formed in the targets by neutron capture of ^{153}Eu (decay product of ^{153}Sm). By keeping the irradiation time rather short, the amounts of this impurity can be kept relatively low compared to the ^{153}Sm activity, allowing the ^{153}Sm to be used without purification from Eu. This is, however, associated with the drawback of a rather short shelf-life of the ^{153}Sm product since the ratio of ^{153}Sm/^{154}Eu decreases significantly with time. To increase the availability of the product, it would be beneficial if the shelf-life could be increased and/or the irradiation time could be prolonged. Therefore, the ^{154}Eu has to be removed from the ^{153}Sm. This, however, is not straightforward since trace amounts of europium have to be removed from large amounts of samarium. Since both are neighbouring lanthanides, the very similar chemical properties have to be taken into account. Moreover, one has to deal with the issues related to the handling of radioactive materials. To minimize the dose rate for the operators, a separation method that could be automatized would be beneficial. Furthermore, the radiation resistance of chemicals and materials that are used in the separation processes is important.

The irradiated solid target is usually first dissolved in highly acidic environment. Afterwards the unwanted by-products can be removed by different separation methods. In this study, the use of *supported ionic liquid phases* (SILPs) for the separation of the aforementioned radiolanthanide pair is investigated. Ionic liquids (ILs) are solvents that consist entirely of ions and they are very interesting alternative for the molecular organic phase in solvent extraction processes. Since bulk ionic liquids are often highly viscous, the kinetics of solvent extraction mechanisms might be rather slow. In SILPs, however, a thin layer of the ionic liquid is immobilized on a high-surface area solid support, leading to faster solvent extraction kinetics. In this study, immobilization of the IL was done physically by impregnation to preserve the properties of the bulk IL. This way, performance of the immobilized and bulk IL can be compared. To prevent high losses of the IL, the hydrophobicity of the IL cation is very important. Since fluorinated ILs have to be prevented, both for radiolysis and waste treatment reasons, hydrophobicity was achieved by using a cation with long alkyl chains. An aromatic group was added to increase the radiation resistivity. To meet the requirements, the IL cation benzyltrioctylammonium was chosen in combination with a chloride or nitrate anion.

Europium has the ability of being relatively stable for a short period of time when being reduced to its divalent state by a strong reducing agent, e.g. by Zn(0). This reduction changes the chemical properties of europium, leading to the possibility to separate europium from the other lanthanides, including neighbouring samarium. Since the properties of Eu(II) are similar to the ones of Sr(II), the latter ion can be used to simulate the behaviour of Eu(II) in the development of the Sm(III)-Eu(II) separation. Therefore, in this investigation the extractability of Sm(III) is compared to the extractability of Sr(II). It was been reported in the literature that Sr(II) can be extracted by crown ethers.[2] Therefore, the use of a crown ether dissolved in the IL phase is studied here for the separation of the Sm(III)-Sr(II) couple. Dicyclohexano-18crown6 (DCH18C6) was chosen because of its high radiation resistivity, good extractability for alkali and alkaline earth ions and a low solubility in water.[2] Sm(III) is hardly extracted, both in bulk and supported IL phases, whilst Sr(II) (and Eu(II)) are partially removed from the aqueous phase, together with Zn(II) in case chemical reduction of europium with Zn(0) was used. When applying this extractant in a SILP using a column setup, it should be possible to separate the Sm(III)-Sr(II) couple, and thus the Sm(III)-Eu(II) couple, eluting Sm(III) first. Sr(II) (and Eu(II)) can be eluted by changing the nitric acid concentration in the mobile phase. Via this method the pure ^{153}Sm radioisotope might be obtained in a faster way compared to separation techniques currently used, where Eu(II) and other possible impurities are eluted first.[3, 4] Moreover, the separation can be performed without the use of any volatile organic solvents.

Since europium has to be reduced during the initial stage of the procedure, it is important that europium stays in its reduced form until separation is achieved. This has the consequence that oxidizing agents, including nitrate, must be avoided in the first part of the separation procedure. Therefore, different extraction conditions were investigated, where mainly the anions in the aqueous and ionic liquid phases are changed. Extraction experiments using stabile isotopes, i.e. Sm(III), Eu(III) and Sr(II) as a simulant for Eu(II), have been conducted from chloride-to-chloride, nitrate-to-nitrate, chloride-to-nitrate and nitrate-to-chloride media to determine the distribution ratios, percentage extraction, separation factors and the kinetics of the extraction. This way, different conditions can be compared to each other to find the optimal extraction parameters.

Complementing radiation stability studies on the ionic liquid phase, both bulk and supported, and the crown ether will provide information about the influence of irradiation on the extraction performance of the investigated system. Other immobilization techniques to create SILPs that eliminates any IL losses (e.g. by chemical immobilization) and the influence of different solid supports will be part of future investigations.

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